

CLAIMS

1. A process for the preparation of "first-generation" random microgels which comprises a stage of controlled radical polymerization of a composition comprising:
- 5
- at least one monoethylenically unsaturated monomer,
  - at least one polyethylenically unsaturated monomer,
  - 10 - a source of free radicals, and
  - a control agent.
2. The process as claimed in claim 1, characterized in that the monoethylenically unsaturated monomer is
- 15
- chosen from:
- styrene and styrene derivatives, such as  $\alpha$ -methylstyrene or vinyltoluene,
  - carboxylic acid vinyl esters, such as vinyl acetate, vinyl Versatate® or vinyl propionate,
  - 20 - vinyl and vinylidene halides,
  - unsaturated ethylenic mono- and dicarboxylic acids, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid or fumaric acid, and the monoalkyl esters of the dicarboxylic acids of
  - 25 the type mentioned with alkanols preferably having 1 to 4 carbon atoms and their N-substituted derivatives,
  - amides of unsaturated carboxylic acids, such as acrylamide, methacrylamide, N-methylolacrylamide, N-methylolmethacrylamide or N-alkylacrylamides,
  - 30 - ethylenic monomers comprising a sulfonic acid group and its alkali metal or ammonium salts, for example vinylsulfonic acid, vinylbenzenesulfonic acid,  $\alpha$ -acrylamidomethylpropanesulfonic acid or 2-
  - 35 sulfoethylene methacrylate,
  - amides of vinylamine, in particular vinylformamide, vinylacetamide, N-vinylpyrrolidone

and N-vinylcaprolactam,  
- unsaturated ethylenic monomers comprising a  
secondary, tertiary or quaternary amino group or a  
heterocyclic group comprising nitrogen, such as,  
5 for example, vinylpyridines, vinylimidazole,  
aminoalkyl (meth)acrylates and  
aminoalkyl (meth)acrylamides, such as  
dimethylaminoethyl acrylate, dimethylaminoethyl  
methacrylate, di(tert-butyl)aminoethyl acrylate,  
10 di(tert-butyl)aminoethyl methacrylate,  
dimethylaminomethylacrylamide or dimethylamino-  
methylethylmethacrylamide, or zwitterionic monomers,  
such as, for example, sulfopropyl(dimethyl)-  
aminopropyl acrylate,  
15 - (meth)acrylic esters, such as glycidyl acrylate or  
glycidyl methacrylate,  
- vinyl nitriles,  
- monomers comprising at least one boronate  
functional group or one precursor, for example  
20 chosen from acryloylbenzeneboronic acid,  
methacryloylbenzeneboronic acid, 4-vinylbenzene-  
boronic acid, 3-acrylamidophenylboronic acid or 3-  
methacrylamidophenylboronic acid, alone or as  
mixtures, or in the form of salts,  
25 - monomers comprising phosphonates, for example  
chosen from N-methacrylamidomethylphosphonic acid  
ester derivatives, in particular the n-propyl  
ester (RN 31857-11-1), the methyl ester (RN 31857-  
12-2), the ethyl ester (RN 31857-13-3), the n-  
30 butyl ester (RN 31857-14-4) or the isopropyl ester  
(RN 51239-00-0), and their phosphonic monoacid and  
diacid derivatives, such as N-methacrylamido-  
methylphosphonic diacid (RN 109421-20-7);  
N-methacrylamidoethylphosphonic acid ester  
35 derivatives, such as N-methacrylamidoethyl-  
phosphonic acid dimethyl ester (RN 266356-40-5) or  
N-methacrylamidoethylphosphonic acid di(2-butyl-  
3,3-dimethyl) ester (RN 266356-45-0), and their  
phosphonic monoacid and diacid derivatives, such

as N-methacrylamidoethylphosphonic diacid (RN 80730-17-2); N-acrylamidomethylphosphonic acid ester derivatives, such as N-acrylamido-methylphosphonic acid dimethyl ester (RN 24610-95-5), N-acrylamidomethylphosphonic acid diethyl ester (RN 24610-96-6) or bis(2-chloropropyl) N-acrylamidomethylphosphonate (RN 50283-36-8), and their phosphonic monoacid and diacid derivatives, such as N-acrylamidomethylphosphonic acid (RN 151752-38-4); the vinylbenzylphosphonate dialkyl ester derivatives, in particular the di(n-propyl) (RN 60181-26-2), di(isopropyl) (RN 159358-34-6), diethyl (RN 726-61-4), dimethyl (RN 266356-24-5), di(2-butyl-3,3-dimethyl) (RN 266356-29-0) and di(t-butyl) (RN 159358-33-5) ester derivatives, and their phosphonic monoacid and diacid alternative forms, such as vinylbenzylphosphonic diacid (RN 53459-43-1); diethyl 2-(4-vinylphenyl)ethanephosphonate (RN 61737-88-0); dialkylphosphonoalkyl acrylate and methacrylate derivatives, such as 2-(acryloyloxy)ethylphosphonic acid dimethyl ester (RN 54731-78-1) and 2-(methacryloyloxy)ethylphosphonic acid dimethyl ester (RN 22432-83-3), 2-(methacryloyloxy)methylphosphonic acid diethyl ester (RN 60161-88-8), 2-(methacryloyloxy)methylphosphonic acid dimethyl ester (RN 63411-25-6), 2-(methacryloyloxy)propylphosphonic acid dimethyl ester (RN 252210-28-9), 2-(acryloyloxy)methylphosphonic acid diisopropyl ester (RN 51238-98-3) or 2-(acryloyloxy)ethylphosphonic acid diethyl ester (RN 20903-86-0), and their phosphonic monoacid and diacid alternative forms, such as 2-(methacryloyloxy)ethylphosphonic acid (RN 80730-17-2), 2-(methacryloyloxy)methylphosphonic acid (RN 87243-97-8), 2-(methacryloyloxy)propylphosphonic acid (RN 252210-30-3), 2-(acryloyloxy)propylphosphonic acid (RN 254103-47-4) and 2-(acryloyloxy)ethylphosphonic acid; vinylphosphonic acid, optionally substituted

by cyano, phenyl, ester or acetate groups,  
vinylidenephosphonic acid, in the sodium salt form  
or the form of its isopropyl ester, or bis(2-  
chloroethyl)vinylphosphonate, it being possible  
5 for these monomers comprising a phosphonic mono-  
or diacid functional group to be used in the  
partially or completely neutralized form,  
optionally neutralized by an amine, for example  
dicyclohexylamine,  
10 - monomers chosen from the phosphate analogs of the  
phosphonate-comprising monomers described above,  
the monomers then comprising a -C-O-P- sequence in  
comparison with the -C-P- sequence of the  
phosphonates, and  
15 - monomers carrying an alkoxysilane group chosen  
from trimethoxysilylpropyl methacrylate,  
triethoxysilylpropyl methacrylate, tributoxy-  
silylpropyl methacrylate,  
dimethoxymethylsilylpropyl methacrylate,  
20 diethoxymethylsilylpropyl methacrylate,  
dibutoxymethylsilylpropyl methacrylate,  
diisopropoxymethylsilylpropyl methacrylate,  
dimethoxysilylpropyl methacrylate,  
diethoxysilylpropyl methacrylate, dibutoxysilyl-  
25 propyl methacrylate, diisopropoxysilylpropyl  
methacrylate, trimethoxysilylpropyl methacrylate,  
triethoxysilylpropyl methacrylate,  
tributoxysilylpropyl methacrylate,  
trimethoxysilylpropyl acrylate, triethoxysilyl-  
30 propyl acrylate, tributoxysilylpropyl acrylate,  
dimethoxymethylsilylpropyl acrylate, diethoxy-  
methylsilylpropyl acrylate, dibutoxymethylsilyl-  
propyl acrylate, diisopropoxymethylsilylpropyl  
acrylate, dimethoxysilylpropyl acrylate, dieth-  
35 oxysilylpropyl acrylate, dibutoxysilylpropyl  
acrylate, diisopropoxysilylpropyl acrylate,  
trimethoxysilylpropyl acrylate, triethoxysilyl-  
propyl acrylate or tributoxysilylpropyl acrylate.

3. The process as claimed in claim 2, characterized in that the monoethylenically unsaturated monomer is chosen from styrene monomers, vinyl esters, neutral or charged hydrophilic acrylates, hydrophobic acrylates, neutral or charged hydrophilic methacrylates, hydrophobic methacrylates, hydrophilic or hydrophobic and neutral or charged acrylamido derivatives or hydrophilic or hydrophobic and neutral or charged methacrylamido derivatives.

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4. The process as claimed in any one of claims 1 to 3, characterized in that the polyethylenically unsaturated monomer is chosen from organic compounds reactive by the radical route comprising at least two ethylenic unsaturations and at most 10 ethylenic unsaturations.

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5. The process as claimed in any one of claims 1 to 4, characterized in that the polyethylenically unsaturated monomer is chosen from acrylic, methacrylic, acrylamido, methacrylamido, vinyl ester, vinyl ether, diene, styrene,  $\alpha$ -methylstyrene and allyl derivatives.

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6. The process as claimed in any one of claims 1 to 5, characterized in that the polyethylenically unsaturated monomer additionally comprises one or more functional groups other than ethylenic unsaturations chosen from the hydroxyl, carboxyl, ester, amide, amino, substituted amino, mercapto, silane, epoxy or halo functional groups.

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7. The process as claimed in any one of claims 1 to 6, characterized in that the polyethylenically unsaturated monomer is chosen from divinylbenzene and divinylbenzene derivatives, vinyl methacrylate, methacrylic acid anhydride, allyl methacrylate, ethylene glycol dimethacrylate, phenylene dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol 200 dimethacrylate,

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- polyethylene glycol 400 dimethacrylate, 1,3-butanediol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, 1,12-dodecanediol dimethacrylate, 1,3-glycerol dimethacrylate, diurethane dimethacrylate or trimethylolpropane trimethacrylate; vinyl acrylate, bisphenol A epoxy diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, polyethylene glycol 600 diacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, neopentyl glycol ethoxylate diacrylate, butanediol diacrylate, hexanediol diacrylate, aliphatic urethane diacrylate, trimethylolpropane triacrylate, trimethylolpropane ethoxylate triacrylate, trimethylolpropane propoxylate triacrylate, glycerol propoxylate triacrylate, aliphatic urethane triacrylate, trimethylolpropane tetraacrylate or dipentaerythritol pentaacrylate; vinyl crotonate, diethylene glycol divinyl ether, 1,4-butanediol divinyl ether or triethylene glycol divinyl ether; diallyl phthalate, diallyldimethylammonium chloride, diallyl maleate, sodium diallyloxyacetate, diallylphenylphosphine, diallyl pyrocarbonate, diallyl succinate, N,N'-diallyltartardiamide, N,N'-diallyl-2,2,2-trifluoroacetamide, the allyl ester of diallyloxyacetic acid, 1,3-diallylurea, triallylamine, triallyl trimesate, triallyl cyanurate, triallyl trimellitate or 1,3,5-triallyltriazine-2,4,6(1H,3H,5H)-trione; N,N'-methylenebisacrylamide, N,N'-methylenebis-methacrylamide, glyoxalbisacrylamide or diacrylamidoacetic acid; divinylbenzene and 1,3-diisopropenylbenzene; butadiene, chloroprene or isoprene.
8. The process as claimed in any one of claims 1 to 7, characterized in that the polyethylenically unsaturated monomer is chosen from N,N'-methylenebisacrylamide, divinylbenzene, ethylene glycol diacrylate or trimethylolpropane triacrylate.

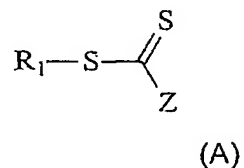
9. The process as claimed in any one of claims 1 to 8, characterized in that the molar fraction of polyethylenically unsaturated monomers with respect to the monoethylenically unsaturated monomers is between 0.001 and 1.

10. The process as claimed in claim 9, characterized in that the molar fraction of polyethylenically unsaturated monomers with respect to the monoethylenically unsaturated monomers is between 0.01 and 1.

11. The process as claimed in any one of claims 1 to 10, characterized in that the controlled radical polymerization is carried out according to a process of Atom Transfer Radical Polymerization (ATRP) type or by a reversible transfer by addition-fragmentation of thiocarbonylthio compounds process.

12. The process as claimed in claim 11, characterized in that the controlled radical polymerization is carried out according to a reversible transfer by addition-fragmentation of thiocarbonylthio compounds process.

13. The process as claimed in claim 12, characterized in that the thiocarbonylthio compounds are compounds of following formula (A):



in which:

- Z represents:
  - . a hydrogen atom,
  - . a chlorine atom,

- . an optionally substituted alkyl radical or an optionally substituted aryl radical,
- . an optionally substituted heterocycle,
- . an optionally substituted alkylthio radical,
- 5 . an optionally substituted arylthio radical,
- . an optionally substituted alkoxy radical,
- . an optionally substituted aryloxy radical,
- . an optionally substituted amino radical,
- . an optionally substituted hydrazine radical,
- 10 . an optionally substituted alkoxycarbonyl radical,
- . an optionally substituted aryloxycarbonyl radical,
- . a carboxyl or optionally substituted acyloxy radical,
- . an optionally substituted aroyloxy radical,
- . an optionally substituted carbamoyl radical,
- 15 . a cyano radical,
- . a dialkyl- or diaryl-phosphonato radical,
- . a dialkyl-phosphinato or diaryl-phosphinato radical, or
- . a polymer chain,
- 20 -  $R_1$  represents:
  - . an optionally substituted alkyl, acyl, aryl, aralkyl, alkenyl or alkynyl group,
  - . an optionally substituted, aromatic, saturated or unsaturated, carbon ring or heterocycle, or
  - 25 . a polymer chain.

14. The process as claimed in claim 12, characterized in that the thiocarbonylthio compounds are xanthate, dithiocarbamate or dithioester compounds carrying a single functional group of formula  $-S(C=S)-$ .

15. The process as claimed in claim 14, characterized in that the compounds are xanthates.

16. A process for the preparation of "second-generation" random microgels, which comprises the following stages:

- 1) the process for the preparation of the first-generation microgel as claimed in any one of



claims 1 to 15 is carried out,

- 2) at least one mono- or polyethylenically unsaturated monomer is added to the microgel obtained in stage 1 in the presence of an activator.

17. A process for the preparation of "nth-generation" random microgels, n being an integer between 2 and 50, which comprises the following stages:

- 1) the process for the preparation of the (n-1)th-generation microgel as claimed in any one of claims 1 to 16 is carried out,  
2) at least one mono- or polyethylenically unsaturated monomer is added to the microgel obtained in stage n-1 in the presence of an activator.

18. The process as claimed in either one of claims 16 and 17 and as claimed in any one of claims 12 to 15, characterized in that the activator is a source of free radicals.

19. A product capable of being obtained by any one of the processes of claims 1 to 18.

20. A star-shaped polymer capable of being obtained by a process for the preparation of an nth-generation microgel, with n between 2 and 50, characterized in that the monomer(s) used in stage n is or are (a) monoethylenically unsaturated monomer(s).

21. The polymer as claimed in claim 20, characterized in that it exhibits (1) a central portion in the form of a first-generation microgel based on a crosslinked polymer resulting from the polymerization of the mono- and polyethylenically unsaturated monomers and (2) arms composed of the monoethylenically unsaturated monomers only added starting from stage 2 as defined above and comprising, at their end, the active part of the control agent (-S(C=S)- functional group), in the case

of a controlled radical polymerization process of reversible transfer by addition-fragmentation of thiocarbonylthio compounds type, or the halogen or pseudohalogen part, in the case of a controlled radical  
5 polymerization process of ATRP type.

22. The polymer as claimed in claims 20 and 21, characterized in that the active part of the control agent ( $-S(C=S)-$  functional group) is substituted in all  
10 or part by a hydrogen atom or a thiol functional group.